

JC18 Rec'd PCT/PTO 05 DEC 2001

<small>FORM PCT 1390 REV. 5/93</small>		<small>U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE</small>	<small>ATTORNEY'S DOCKET NO.</small> RUDINGER ET AL-5 (PCT)
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			<small>U.S. APPLICATION NO. (if known, see 37 CFR 1.5)</small> 10/009507
<small>INTERNATIONAL APPLICATION NO.</small> PCT/EP 00/06092	<small>INTERNATIONAL FILING DATE</small> 29 JUNE 2000	<small>PRIORITY DATE CLAIMED</small> JULY 22, 1999	
<small>TITLE OF INVENTION</small> PROCESS FOR THE SEPARATION AND PURIFICATION OF AN AQUEOUS MIXTURE COMPRISING THE MAIN COMPONENTS ACETIC ACID AND FORMIC ACID			
<small>APPLICANT(S) FOR DO/EO/US</small> Christoph RUDINGER et al			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<div>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</div> <div>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</div> <div>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371 (f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).</div> <div>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</div> <div>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))<div>a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau)</div><div>b. <input type="checkbox"/> has been transmitted by the International Bureau.</div><div>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</div></div> <div>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</div> <div>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).<div>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</div><div>b. <input type="checkbox"/> have been transmitted by the International Bureau.</div><div>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</div><div>d. <input type="checkbox"/> have not been made and will not be made.</div></div> <div>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</div> <div>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</div> <div>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</div> <div>Items 11. to 16. below concern other document(s) or information included:<div>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</div><div>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</div><div>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</div><div>14. <input type="checkbox"/> A substitute specification.</div><div>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</div><div>16. <input checked="" type="checkbox"/> Other items or information:</div></div> <div>PCT/ISA/210 - Int'l. Search Report (English) 3 SHEETS OF FORMAL DRAWINGS</div> <div>Applicant Claims Priority under 35 U.S.C. §119 of German (country) Application No. 19934410.8 filed July 22, 1999 Applicant Claims Priority under 35 U.S.C. §120 PCT No. PCT/EP00/06092 filed June 29, 2000.</div>			

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: CHRISTOPH RÜDINGER (PCT) - 5
PCT No.: PCT/EP 00/06092 FILED: JUNE 29, 2000
TITLE: PROCESS FOR THE SEPARATION AND PURIFICATION OF
AN AQUEOUS MIXTURE COMPRISING THE MAIN COMPONENTS
ACETIC ACID AND FORMIC ACID

PRELIMINARY AMENDMENT

BOX PCT
U.S. Patent and Trademark Office
P.O. Box 2327
Arlington, VA 22202

Dear Sir:

Preliminary to Examination, please amend the above-
identified application as follows:

IN THE ABSTRACT:

Please insert the Abstract attached hereto on its own
separate page.

IN THE SPECIFICATION

On page 1, below the title, and above line 1, please insert
as follows:

conveying the extract stream to a solvent distillation column (8) from which, in a first step, a mixture (A) comprising water and solvent is separated off via the top and a mixture (B) comprising acetic acid, formic acid and high boilers is separated off via the bottom, separating the formic acid off from the mixture (B) in column (29) and subsequently fractionating the remaining mixture (B) into pure acetic acid and high boilers in an acetic acid distillation column (5), and conveying the mixture (A) to a phase separator (25) from which the resulting aqueous phase containing residual solvent is recirculated to the solvent stripping column (11) and the organic phase is recirculated to the extractor (7).--

On Page 6, above line 1, please insert:

--BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an apparatus for carrying out the separation and purification process of the invention;

FIG. 2 shows the apparatus of FIG. 1 plus a recirculation back to the extractor; and

FIG. 3 shows the apparatus of FIG. 1 plus a formic acid distillation column.--

On Page 11, between lines 13 and 14, please insert:

--DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS--

A Marked-Up Version of Pages 1, 4, 5, 6 and 11 is enclosed.

IN THE CLAIMS:

Please cancel claims 1 to 17 without prejudice, and please add new claims 18 to 34 as follows:

18. Process for the separation and purification of an aqueous mixture comprising main components acetic acid, formic acid and high boilers by extraction with a solvent in a circulation process, which comprises

feeding a raffinate stream containing a major part of water to a solvent stripping column (11) for removal of the water;

conveying an extract stream to a solvent distillation column (8) from which, in a first step, a mixture (A) comprising water and solvent is separated off via a top of column (8) and a mixture (B) comprising acetic acid, formic acid and high boilers is separated off via a bottom of column (8);

separating the formic acid off from the mixture (B) in column (29) and subsequently fractionating a remaining mixture (B) into pure acetic acid and high boilers in an acetic acid distillation column (5), and

conveying the mixture (A) to a phase separator (25) from which an aqueous phase containing residual solvent is recirculated to the solvent stripping column (11) and an organic phase is recirculated to an extractor (7).

19. Process according to Claim 18, comprising operating the solvent distillation column (8) under atmospheric pressure.

20. Process according to Claim 18, comprising operating the solvent distillation column (8) under a superatmospheric pressure of from $1 \cdot 10^5$ to $50 \cdot 10^5$ Pa.

21. Process according to Claim 18, comprising operating the extractor (7) in at least one stage.

22. Process according to Claim 18,

wherein a solvent circuit in the extractor (7) runs countercurrent to crude acid.

23. Process according to Claim 18,

wherein the solvent used is selected from the group consisting of a saturated hydrocarbon having from 4 to 8 carbon atoms, an unsaturated hydrocarbon having from 4 to 8 carbon atoms, a cyclic hydrocarbon having from 4 to 8 carbon atoms, and mixtures thereof.

24. Process according to Claim 18,

wherein the solvent used is at least one compound selected from the group consisting of ethers, esters, ketones, hydrocarbons and alcohols.

25. Process according to Claim 18,

wherein the solvent used is at least one compound selected from the group consisting of methyl tert-butyl ether, diisopropyl ether, di-n-propyl ether, ethyl butyl ether, ethyl acetate and isopropyl acetate.

26. Process according to Claim 18, comprising

fractionated in an intermediate distillation column (29) into a bottom product which is free of formic acid and comprises acetic acid and high boilers and a mixed top product comprising formic acid, water and small amounts of acetic acid;

where a bottom product from column (29) is fractionated in a downstream acetic acid distillation column (5) into pure acetic acid and high boilers and a top product from column (29) is fed to a pure formic acid distillation column (33) where it is fractionated into pure formic acid as top product and a mixed bottom product comprising acetic acid, formic acid and water which is recirculated to an extract stream to the solvent distillation column (8).

32. Process according to Claim 31, comprising
operating the pure formic acid distillation column (33)
at a pressure which is from $0.1 \cdot 10^5$ to $25 \cdot 10^5$ Pa lower than a
pressure in the intermediate distillation column (29).

33. Process according to Claim 18,
wherein heat of condensation in the distillation column
(29) is used selected from the group consisting of heating the
formic acid distillation column (33), heating the solvent

distillation column (11), and heating both column (33) and column 11).

34. Process according to Claim 18,

wherein the heat of reaction of the upstream reaction (for example a catalytic gas-phase oxidation of hydrocarbons) is used for heating at least one selected from the group consisting of the solvent distillation column (8), the distillation column (29), the acetic acid distillation column (5) and the formic acid distillation column (33).

REMARKS

By this Preliminary Amendment, the Specification has been amended to include a cross-reference to related applications which has been inserted in page 1. Also pages 1, 4, 6 and 11 have been amended to recite the Specification section headings required by U.S. practice. Page 5 was amended to include a revision made in the International Office.

The amendments to the claims are to cancel the originally filed claims 1 to 17 without prejudice, and to rewrite these

claims as new claims 18 to 34, respectively. New claims 18 to 34 eliminate the multiple dependency of the claims, so as to avoid the U.S.P.T.O. surcharge therefor. Also claims 18 to 34 have been written so as to comply with U.S. formal requirements, and include changes made in the International Office.

No new matter has been introduced by this amendment. Entry of this amendment is respectfully requested.

Respectfully submitted,

CHRISTOPH RÜDINGER (PCT) - 5

By: Edward R. Freedman
 Allison C. Collard, Reg. No. 22,532
 Edward R. Freedman, Reg. No. 26,048
 Attorneys for Applicant

COLLARD & ROE, P.C.
 1077 Northern Boulevard
 Roslyn, New York 11576
 (516) 365-9802

ERF/mt

Enclosure: (1) Abstract of the Disclosure.

(2) Marked-Up Version of Amended Specification pages
 1, 4, 5, 6 and 11.

EXPRESS MAIL # EL 871 450 163 US

DATE: December 5, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, on the date indicated above, and is addressed to Box PCT, U.S. Patent and Trademark Office, P.O. Box 2327, Arlington, VA 22202.

Lisa L. Vulpis
 Lisa L. Vulpis

(continued)

Figure 1. Schematic representation of the experimental design. The first part of the experiment consisted of a 10-min habituation period, followed by a 10-min baseline period, and then a 10-min test period. The second part of the experiment consisted of a 10-min habituation period, followed by a 10-min baseline period, and then a 10-min test period. The third part of the experiment consisted of a 10-min habituation period, followed by a 10-min baseline period, and then a 10-min test period. The fourth part of the experiment consisted of a 10-min habituation period, followed by a 10-min baseline period, and then a 10-min test period. The fifth part of the experiment consisted of a 10-min habituation period, followed by a 10-min baseline period, and then a 10-min test period. The sixth part of the experiment consisted of a 10-min habituation period, followed by a 10-min baseline period, and then a 10-min test period. The seventh part of the experiment consisted of a 10-min habituation period, followed by a 10-min baseline period, and then a 10-min test period. The eighth part of the experiment consisted of a 10-min habituation period, followed by a 10-min baseline period, and then a 10-min test period. The ninth part of the experiment consisted of a 10-min habituation period, followed by a 10-min baseline period, and then a 10-min test period. The tenth part of the experiment consisted of a 10-min habituation period, followed by a 10-min baseline period, and then a 10-min test period.

MARKED-UP VERSION
OF
AMENDED SPECIFICATION

WO 01/07391

PCT/EP00/06092

Process for the separation and purification of an aqueous mixture comprising the main components acetic acid and formic acid

CROSS REFERENCE TO RELATED APPLICATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a process for the separation and purification of an aqueous reaction mixture comprising the main components acetic acid and formic acid.

2. The Prior Art

The preparation of acetic acid by catalytic oxidation of saturated and/or unsaturated hydrocarbons, for example the gas-phase oxidation of C₄-hydrocarbons, results in formation of product streams comprising as main components acetic acid, formic acid and water in varying proportions.

To work them up further, these product streams have to be separated into their individual components. Separation of a ternary acid/water mixture comprising acetic acid, formic acid and water into its pure components by distillation, for example, presents considerable problems since the system contains not only the binary water/formic acid maximum azeotrope but also a ternary water/formic acid/acetic acid saddle azeotrope.

If such a mixture has a high water concentration, separation by distillation has a tremendous additional energy requirement since all the water has to be distilled off at the top of a column as lowest-boiling component.

- 4 -

about 7% by weight of benzene. The use of benzene in this process and the residual benzene content in the formic acid make this process unattractive.

All the processes known from the prior art are either only suitable for satisfactorily separating binary mixtures such as acetic acid/water, formic acid/water and acetic acid/formic acid or only economically applicable to aqueous acid mixtures in which a high concentration of acid (>60% by weight) is present. Furthermore, some of the known processes are no longer acceptable from the point of view of today's safety and environmental standards because of their use of benzene or chlorinated hydrocarbons.

SUMMARY OF THE INVENTION

12 It is therefore an object of the invention to provide
13 a process for the separation of a ternary, aqueous mixture of acids into its pure components, which process does not have the disadvantages mentioned in the discussion of the prior art.

It has now been found that the separation and purification of a mixture comprising the main components acetic acid, formic acid, water and high boilers (hereinafter referred to as crude acid) can be carried out particularly readily if the mixture is extracted by means of a solvent in a circulation process in a first step and the extract stream consisting predominantly of solvent, acetic acid, formic acid, high boilers and water is subsequently fractionated in

- 5 -

a sequence of distillation steps into the constituents solvent which is recirculated to the extraction, water, formic acid, acetic acid and high boilers, and the raffinate stream is freed of solvent in a further distillation step by means of a solvent stripping column.

6 The invention provides a process for the separation and purification of an aqueous mixture comprising the main components acetic acid, formic acid and high boilers by extraction with a solvent in a circulation process, which comprises feeding the raffinate stream containing a major part of the water to a solvent stripping column (11) for removal of the water and conveying the extract stream to a solvent distillation column (8) from which, in a first step, a mixture (A) comprising water and solvent is separated off via the top and a mixture (B) comprising acetic acid, formic acid and high boilers is separated off via the bottom, separating the formic acid off from the mixture (B) in column (29) and subsequently fractionating the remaining mixture (B) into pure acetic acid and high boilers in an acetic acid distillation column ⁽⁵⁾ and conveying the mixture (A) to a phase separator (25) from which the resulting aqueous phase containing residual solvent is recirculated to the solvent stripping column (11) and the organic phase is recirculated to the extractor (7).

24

BRIEF DESCRIPTION OF THE DRAWINGS

- 6 -

In the first step (extraction) of the process of the invention (Fig. 1), the crude acid feed comprising varying proportions of acetic acid, formic acid, water and high boilers is fed via a line (6) to an extractor (7) and brought into contact with a solvent. The extractor (7) can have a single-stage or preferably multistage configuration. The solvent stream can, in this process, be directed in the direction of flow of the crude acid or preferably be conveyed in countercurrent to the crude acid. Solvents which can be used here are ethers, esters, ketones, alcohols, saturated, unsaturated and cyclic hydrocarbons having from 4 to 8 carbon atoms and their mixtures, preferably ethers and esters having from 4 to 7 carbon atoms, particularly preferably methyl tert-butyl ether, diisopropyl ether, di-n-propyl ether, ethyl butyl ether, ethyl acetate and isopropyl acetate, in a mixing ratio to crude acid (volume/volume) of from 0.5 to 20, preferably from 1 to 5, particularly preferably from 1.5 to 3.5 (ratio volume/volume). The extraction can take place in a temperature and pressure range in which the extraction solvent and the crude acid are present in liquid form and as separate phases, i.e. with a miscibility gap. Preference is given to a temperature range from 0°C to 60°C and a pressure range from $1 \cdot 10^5$ to $20 \cdot 10^5$ Pa.

The raffinate obtained from the extractor (7) is fed via line (15) to the solvent stripping column (11) where pure

- 11 -

additional pure formic acid distillation (33) under lower pressure than in the separation column (29). This results in a significant energy saving together with greatly improved formic acid purity compared with comparable processes. Furthermore, the heat of condensation of the distillation column (29) can be used in an integrated heat system for heating the formic acid distillation column (33) and the solvent column (11). The heat of reaction of the reactions preceding this separation process, for example a catalytic gas-phase oxidation of hydrocarbons, can likewise be used for heating the solvent distillation column (8), the distillation column (29), the formic acid distillation column (33) and the acetic acid distillation column (5).

13
14 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples illustrate the process of the invention with reference to the figures:

Example 1:

In an apparatus corresponding to the embodiment of Fig. 3, a crude acid stream comprising 12.9 kg/h of acetic acid, 2.6 kg/h of formic acid, 48.4 kg/h of water and 0.8 kg/h of high boilers was fed via line (6) to the extractor (7) (countercurrent extraction column with stationary stainless steel packing, organic phase dispersed). Via line (27) and line (14), a solvent return stream containing 135.4 kg/h of methyl tert-butyl ether (MTBE),

3/parts

WO 01/07391

PCT/EP00/06092

Process for the separation and purification of an aqueous mixture comprising the main components acetic acid and formic acid

The invention relates to a process for the separation and purification of an aqueous reaction mixture comprising the main components acetic acid and formic acid.

The preparation of acetic acid by catalytic oxidation of saturated and/or unsaturated hydrocarbons, for example the gas-phase oxidation of C₄-hydrocarbons, results in formation of product streams comprising as main components acetic acid, formic acid and water in varying proportions.

To work them up further, these product streams have to be separated into their individual components. Separation of a ternary acid/water mixture comprising acetic acid, formic acid and water into its pure components by distillation, for example, presents considerable problems since the system contains not only the binary water/formic acid maximum azeotrope but also a ternary water/formic acid/acetic acid saddle azeotrope.

If such a mixture has a high water concentration, separation by distillation has a tremendous additional energy requirement since all the water has to be distilled off at the top of a column as lowest-boiling component.

- 2 -

For the separation of aqueous mixtures having an acetic acid content of >60% by weight and a formic acid content of 5% by weight, Hunsmann and Simmrock (Chemie-Ing.-Tech., 38, 1966) recommend the use of azeotropic distillation for making the separation easier and for reducing the energy required. As azeotropic entrainer for the removal of water, ethyl n-butyl ether is proposed. The azeotrope of water and entrainer boils at about 91°C and contains about 10% by weight of water. The entrainer ethyl n-butyl ether forms no azeotrope with formic acid and acetic acid.

For separating off formic acid, DE-A 1204214 recommends azeotropic rectification using n-butyl chloride as entrainer. The disadvantage of this process is the use of chlorinated hydrocarbons as entrainer.

US-A 5633402 discloses a process for the separation of binary mixtures of formic acid and acetic acid by means of azeotropic distillation. Methyl formate is used as entrainer for the formic acid. Removal of water is not described in this process.

DE-A 4426132, EP-A 0635474, DE-A 19610356 (US-A 5662780) disclose various processes for the purification and dewatering of acetic acid by means of azeotropes with various entrainers. However, none of these processes describes the dewatering of a mixture of acetic acid and formic acid.

- 3 -

US-A 5173156, US-A 5006205, US-A 4877490 and US-A 4935100 disclose processes for the dewatering of formic acid by means of extractive rectification. Entrainers mentioned here are, for example, cyclohexanone, oxalic acid, decanoic acid and methyl salicylate.

EP-A 156309 (CA-A 1238919) and EP-A 12321 (US-A 4262140) describe the dewatering of formic acid by extractive rectification using carboxamides as auxiliaries. However, none of these processes describes the dewatering of a mixture of acetic acid and formic acid.

The "Process Economics Program" Report No. 37A (1973) of the Stanford Research Institute discloses a process for the separation of an aqueous mixture comprising about 42% by weight of acetic acid and 2% by weight of formic acid. In this process, the aqueous mixture is concentrated by countercurrent extraction with diisopropyl ether. In the dewatering and solvent recovery column, the water is distilled off at the top as an azeotrope of water and diisopropyl ether. The bottom product, namely a mixture of acetic acid and formic acid containing about 0.12% by weight of water, is fractionated further by azeotropic rectification. Benzene is used as entrainer for the formic acid. A great disadvantage of this process is the low quality of the formic acid separated off, which still contains about 1% by weight of acetic acid, about 2% by weight of water and

- 4 -

about 7% by weight of benzene. The use of benzene in this process and the residual benzene content in the formic acid make this process unattractive.

All the processes known from the prior art are either only suitable for satisfactorily separating binary mixtures such as acetic acid/water, formic acid/water and acetic acid/formic acid or only economically applicable to aqueous acid mixtures in which a high concentration of acid (>60% by weight) is present. Furthermore, some of the known processes are no longer acceptable from the point of view of today's safety and environmental standards because of their use of benzene or chlorinated hydrocarbons.

It is therefore an object of the invention to provide a process for the separation of a ternary, aqueous mixture of acids into its pure components, which process does not have the disadvantages mentioned in the discussion of the prior art.

It has now been found that the separation and purification of a mixture comprising the main components acetic acid, formic acid, water and high boilers (hereinafter referred to as crude acid) can be carried out particularly readily if the mixture is extracted by means of a solvent in a circulation process in a first step and the extract stream consisting predominantly of solvent, acetic acid, formic acid, high boilers and water is subsequently fractionated in

- 5 -

a sequence of distillation steps into the constituents solvent which is recirculated to the extraction, water, formic acid, acetic acid and high boilers, and the raffinate stream is freed of solvent in a further distillation step by means of a solvent stripping column.

The invention provides a process for the separation and purification of an aqueous mixture comprising the main components acetic acid, formic acid and high boilers by extraction with a solvent in a circulation process, which comprises feeding the raffinate stream containing a major part of the water to a solvent stripping column (11) for removal of the water and conveying the extract stream to a solvent distillation column (8) from which, in a first step, a mixture (A) comprising water and solvent is separated off via the top and a mixture (B) comprising acetic acid, formic acid and high boilers is separated off via the bottom, separating the formic acid off from the mixture (B) in column (29) and subsequently fractionating the remaining mixture (B) into pure acetic acid and high boilers in an acetic acid distillation column, and conveying the mixture (A) to a phase separator (25) from which the resulting aqueous phase containing residual solvent is recirculated to the solvent stripping column (11) and the organic phase is recirculated to the extractor (7).

- 6 -

In the first step (extraction) of the process of the invention (Fig. 1), the crude acid feed comprising varying proportions of acetic acid, formic acid, water and high boilers is fed via a line (6) to an extractor (7) and brought into contact with a solvent. The extractor (7) can have a single-stage or preferably multistage configuration. The solvent stream can, in this process, be directed in the direction of flow of the crude acid or preferably be conveyed in countercurrent to the crude acid. Solvents which can be used here are ethers, esters, ketones, alcohols, saturated, unsaturated and cyclic hydrocarbons having from 4 to 8 carbon atoms and their mixtures, preferably ethers and esters having from 4 to 7 carbon atoms, particularly preferably methyl tert-butyl ether, diisopropyl ether, di-n-propyl ether, ethyl butyl ether, ethyl acetate and isopropyl acetate, in a mixing ratio to crude acid (volume/volume) of from 0.5 to 20, preferably from 1 to 5, particularly preferably from 1.5 to 3.5 (ratio volume/volume). The extraction can take place in a temperature and pressure range in which the extraction solvent and the crude acid are present in liquid form and as separate phases, i.e. with a miscibility gap. Preference is given to a temperature range from 0°C to 60°C and a pressure range from $1 \cdot 10^5$ to $20 \cdot 10^5$ Pa.

The raffinate obtained from the extractor (7) is fed via line (15) to the solvent stripping column (11) where pure

- 7 -

water is taken off at the bottom (line (13)). The product from the top of the solvent stripping column is fed to a phase separator (9). The aqueous phase obtained there goes via line (10) back to the top of the solvent stripping column (11), while the organic phase obtained is recirculated via line (14) to the extractor (7).

The extract taken off from the extractor (7), comprising varying proportions of solvent, acetic acid, formic acid, water and high boilers, is conveyed from the extractor to a solvent distillation column (8).

The solvent distillation column (8) can be operated under atmospheric pressure, but preferably under superatmospheric pressure.

The solvent distillation column (8) is preferably operated under a pressure of $1 \cdot 10^5$ to $50 \cdot 10^5$ Pa, preferably from $1 \cdot 10^5$ to $25 \cdot 10^5$ Pa, particularly preferably from $1 \cdot 10^5$ to $5 \cdot 10^5$ Pa.

In this column, the extract is divided into two substreams by distillation. One substream (mixture (A)), comprising a mixture of solvent and water, is taken off at the top of the column and fed to a phase separator (25) (line (24)). The aqueous phase containing residual solvent is separated off via line (26), and fed to the solvent stripping column (11), preferably at the feed point of the raffinate. The organic

- 8 -

phase is taken off via line (27) and recirculated to the extractor (7).

The second substream (mixture (B)) obtained from column (8), comprising the components acetic acid, formic acid and high boilers, is taken off at the bottom of the solvent distillation column (8) and introduced into an intermediate distillation column (29) (line 28)). The column (29) is likewise operated under atmospheric pressure, but preferably under superatmospheric pressure of from $1 \cdot 10^5$ to $50 \cdot 10^5$ Pa, more preferably from $1 \cdot 10^5$ to $25 \cdot 10^5$ Pa, particularly preferably from $1 \cdot 10^5$ to $5 \cdot 10^5$ Pa. From this column (29), the pure formic acid is taken off at the top via line (19). A mixture of acetic acid and high boilers which is free of formic acid is taken off at the bottom and conveyed via line (31) to an acetic acid distillation column (5) in which the remaining stream is fractionated into pure acetic acid and high boilers. The acetic acid is taken off at the top via line (17) and the high boilers are separated off at the bottom of the column via line (18).

In a particular embodiment (Fig. 2) of the process of the invention, the solvent distillation column (8) is operated in such a way that part of the water is also carried out at the bottom via line (28) and is conveyed together with the acetic acid, the formic acid and the high boilers to the intermediate distillation column (29). In this case, the

- 9 -

water containing small amounts of acetic acid and formic acid is taken off from the distillation column (29) via an additional side offtake and line (35) and is discarded or recirculated via line (35) to the crude acid inlet (6) or another point on the extractor (7).

In this embodiment, the separation function in the solvent column (8) is significantly simplified compared to the process shown in Fig. 1 by the codischarge of water. Furthermore, the additional side offtake on the formic acid distillation column (29) also simplifies the separation into pure formic acid and the bottom product comprising acetic acid and high boilers.

In a further embodiment (Fig. 3) of the process of the invention, the solvent distillation column (8) is likewise operated in such a way that the substream (mixture (B)) separated off at the bottom via line (28) still contains small amounts of water in order to make the separation easier.

This bottom product, comprising acetic acid, formic acid and small amounts of water, is fractionated in an intermediate distillation column (29) into a bottom product which comprises acetic acid and high boilers and is free of formic acid and a mixed top product comprising formic acid, water and small amounts of acetic acid.

- 10 -

The product from the top of the distillation column (29), comprising formic acid, water and small amounts of acetic acid, is subsequently conveyed via line (19) to the pure formic acid distillation column (33). This column (33) is operated at a lower pressure than the intermediate distillation column (29). The pressure difference between column (33) and column (29) is from $0.1 \cdot 10^5$ Pa to $25 \cdot 10^5$ Pa, preferably from $0.5 \cdot 10^5$ Pa to $5 \cdot 10^5$ Pa. In the pure formic acid distillation column (33), the product stream is fractionated into pure formic acid via line (34) as top product and a mixed bottom product comprising acetic acid, formic acid and water. This bottom product is recirculated via line (32) to the extract stream or another feed point on the solvent distillation column (8).

The raffinate stream (15) from the extractor (7) and the aqueous phase (26) from the phase separation vessel (25) are conveyed to the solvent stripping column (11). Pure water is taken off at the bottom of this column via line (13). The product from the top of this column is conveyed to the phase separator (9). The organic phase obtained is recirculated to the extractor (7), and the aqueous phase is fed into the top of the stripper column (11) via line (10).

In this process variant, it is of great advantage that the demands made of the separation efficiency of the separation column (29) are significantly reduced by the

- 11 -

additional pure formic acid distillation (33) under lower pressure than in the separation column (29). This results in a significant energy saving together with greatly improved formic acid purity compared with comparable processes. Furthermore, the heat of condensation of the distillation column (29) can be used in an integrated heat system for heating the formic acid distillation column (33) and the solvent column (11). The heat of reaction of the reactions preceding this separation process, for example a catalytic gas-phase oxidation of hydrocarbons, can likewise be used for heating the solvent distillation column (8), the distillation column (29), the formic acid distillation column (33) and the acetic acid distillation column (5).

The following examples illustrate the process of the invention with reference to the figures:

Example 1:

In an apparatus corresponding to the embodiment of Fig. 3, a crude acid stream comprising 12.9 kg/h of acetic acid, 2.6 kg/h of formic acid, 48.4 kg/h of water and 0.8 kg/h of high boilers was fed via line (6) to the extractor (7) (countercurrent extraction column with stationary stainless steel packing, organic phase dispersed). Via line (27) and line (14), a solvent return stream containing 135.4 kg/h of methyl tert-butyl ether (MTBE),

- 12 -

4.0 kg/h of water, 0.5 kg/h of acetic acid and 0.2 kg/h of formic acid was fed to the extractor (7) in the steady state. The extract stream leaving the extractor (7) was composed of 133.9 kg/h of MTBE, 13.1 kg/h of acetic acid, 8.1 kg/h of water, 2.6 kg/h of formic acid and 0.1 kg/h of high boilers. The raffinate stream leaving the extractor (7) via line (15) was composed of 44.7 kg/h of water, 1.5 kg/h of MTBE, 0.4 kg/h of acetic acid, 0.2 kg/h of formic acid and 0.7 kg/h of high boilers.

The solvent distillation column (8) and the distillation column (29) were operated at a pressure of 2.75×10^5 Pa. The pure formic acid column (33) and the pure acetic acid column (5) were operated at a pressure of 1×10^5 Pa.

At the bottom of the solvent column (8), a stream comprising 13.4 kg/h of acetic acid, 3.7 kg/h of formic acid, 0.2 kg/h of water and 0.1 kg/h of high boilers was taken off at a temperature of 147°C via line (28). From the phase separator (25), which was connected to the top of column (8) via line (24), an organic phase comprising 133.8 kg/h of MTBE, 0.5 kg/h of acetic acid, 0.2 kg/h of formic acid and 4.1 kg/h of water was recirculated via line (27) to the solvent inlet of the extractor (7). The stream of aqueous phase leaving the phase separator via line (26) was composed

- 13 -

of 0.03 kg/h of acetic acid, 0.01 kg/h of formic acid, 4.1 kg/h of water and 0.1 kg/h of MTBE.

At the bottom of the distillation column (29), a stream comprising 12.6 kg/h of acetic acid and 0.1 kg/h of high boilers was taken off at a temperature of 154.1°C via line (31). At the bottom of the pure acetic acid column (5), a stream comprising 0.06 kg/h of acetic acid and 0.1 kg/h of high boilers was taken off at a temperature of 143.6°C via line (18).

The stream leaving the top of the pure formic acid column (33) via line (34) comprised 2.4 kg/h of formic acid. From the bottom of the pure formic acid column (33), a stream comprising 0.8 kg/h of acetic acid, 1.3 kg/h of formic acid and 0.2 kg/h of water was taken off at a temperature of 106.2°C and recirculated via line (32) to the inlet of the solvent distillation column (8).

The aqueous stream leaving the bottom of the solvent stripping column (11) via line (13) comprised 48.4 kg/h of water, 0.4 kg/h of acetic acid, 0.2 kg/h of formic acid and 0.7 kg/h of high boilers. The return stream of organic phase via line (14) from the phase separation vessel (9) of the solvent stripper (11) to the solvent inlet of the extractor (7) was composed of 1.6 kg/h of MTBE, 0.01 kg/h of acetic acid, 0.01 kg/h of formic acid and 0.05 kg/h of water.

- 14 -

Fractionation of the crude acid mixture into 2.4 kg/h of 99.9% purity by weight formic acid, 12.5 kg/h of 99.9% purity by weight acetic acid and 49.6 kg/h of 97.5% purity by weight water required, without preheating of the feed upstream of the distillation columns, the following energy input:

bottom heating of the solvent distillation column (8): 20.5 kW

bottom heating of the separation column (29): 10 kW

bottom heating of the pure formic acid column (33): 5 kW

bottom heating of the pure acetic acid column (5): 3.4 kW

bottom heating of the solvent stripping column (11): 4 kW

The total of 43 kW corresponds to 2.87 kW per kg of acid.

Example 2:

In an apparatus corresponding to the embodiment shown in Fig. 3, a crude acid stream comprising 12.9 kg/h of acetic acid, 2.6 kg/h of formic acid, 48.4 kg/h of water and 0.8 kg/h of high boilers was fed via line (6) to the extractor (7) (countercurrent extraction column with stationary stainless steel packing, organic phase dispersed). A solvent return stream comprising 135.4 kg/h of methyl tert-butyl ether (MTBE), 4.0 kg/h of water, 0.5 kg/h of acetic acid and 0.2 kg/h of formic acid was fed to the extractor (7) via line (27) and line (14). The extract stream leaving the

- 15 -

extractor (7) was composed of 133.9 kg/h of MTBE, 13.1 kg/h of acetic acid, 8.1 kg/h of water, 2.6 kg/h of formic acid and 0.1 kg/h of high boilers. The raffinate stream leaving the extractor (7) via line (15) was composed of 44.6 kg/h of water, 1.5 kg/h of MTBE, 0.4 kg/h of acetic acid, 0.2 kg/h of formic acid and 0.7 kg/h of high boilers.

The solvent distillation column (8) and the distillation column (29) were operated at a pressure of 1.0×10^5 Pa. The pure formic acid column (33) was operated at a pressure of 0.25×10^5 Pa. The pure acetic acid column (5) was operated at a pressure of 1×10^5 Pa.

At the bottom of the solvent column (8), a stream comprising 13.4 kg/h of acetic acid, 3.7 kg/h of formic acid, 0.2 kg/h of water and 0.1 kg/h of high boilers was discharged at a temperature of 110°C via line (28). From the phase separator (25), which was connected to the top of the column (8) via line (24), an organic phase comprising 133.8 kg/h of MTBE, 0.5 kg/h of acetic acid, 0.2 kg/h of formic acid and 4.0 kg/h of water was recirculated via line (27) to the solvent inlet of the extractor (7). The stream of aqueous phase leaving the phase separator via line (26) was composed of 0.03 kg/h of acetic acid, 0.01 kg/h of formic acid, 4.0 kg/h of water and 0.1 kg/h of MTBE.

At the bottom of the distillation column (29), a stream comprising 12.6 kg/h of acetic acid and 0.1 kg/h of

- 16 -

high boilers was taken off at a temperature of 117.8°C via line (31). At the bottom of the pure acetic acid column (5), a stream comprising 0.1 kg/h of acetic acid and 0.1 kg/h of high boilers was taken off at a temperature of 143.6°C via line (18).

The stream leaving the top of the pure formic acid column (33) via line (34) comprised 2.4 kg/h of formic acid. A stream comprising 0.8 kg/h of acetic acid, 1.3 kg/h of formic acid and 0.2 kg/h of water was taken off at the bottom of the pure formic acid column (33) at a temperature of 68.6°C and recirculated via line (32) to the inlet of the solvent distillation column (8).

The aqueous stream leaving the bottom of the solvent stripper column (11) via line (13) comprised 48.4 kg/h of water, 0.4 kg/h of acetic acid, 0.2 kg/h of formic acid and 0.7 kg/h of high boilers. The return stream of organic phase via line (14) from the phase separation vessel (9) of the solvent stripper (11) to the solvent inlet of the extractor (7) was composed of 1.6 kg/h of MTBE, 0.01 kg/h of acetic acid, 0.01 kg/h of formic acid and 0.01 kg/h of water.

Fractionation of the crude acid mixture into 2.4 kg/h of 99.9% purity by weight formic acid, 12.5 kg/h of 99.9% purity by weight acetic acid and 49.6 kg/h of 97.5% purity by weight water required, without preheating of the feed

- 17 -

upstream of the distillation columns, the following energy input:

bottom heating of the solvent distillation column (8): 30 kW

bottom heating of the separation column (29): 18 kW

bottom heating of the pure formic acid column (33): 3 kW

bottom heating of the pure acetic acid column (5): 5 kW

bottom heating of the solvent stripping column (11): 4.5 kW

The total of 60.5 kW corresponds to 4.05 kW per kg of acid.

Example 3:

In an apparatus corresponding to the variant shown in Fig. 2, a crude acid stream comprising 12.8 kg/h of acetic acid, 2.5 kg/h of formic acid, 48.6 kg/h of water and 0.8 kg/h of high boilers was fed via line (6) to the extractor (7) (countercurrent extraction column with stationary stainless steel packing, organic phase dispersed). A solvent return stream comprising 179.7 kg/h of methyl tert-butyl ether (MTBE), 1.9 kg/h of water, 0.4 kg/h of acetic acid and 0.1 kg/h of formic acid was fed to the extractor (7) via line (27) and line (14). The extract stream leaving the extractor (7) was composed of 178.3 kg/h of MTBE, 13.1 kg/h of acetic acid, 9.8 kg/h of water, 2.6 kg/h of formic acid and 0.2 kg/h of high boilers. The raffinate stream leaving the extractor (7) via line (15) was composed of 40.7 kg/h of

- 18 -

water, 1.3 kg/h of MTBE, 0.2 kg/h of acetic acid, 0.1 kg/h of formic acid and 0.6 kg/h of high boilers.

The solvent distillation column (8) and the distillation column (29) were operated at a pressure of $2.75 \cdot 10^5$ Pa. The pure acetic acid column (5) was operated at a pressure of $1 \cdot 10^5$ Pa.

At the bottom of the solvent column (8), a stream comprising 12.6 kg/h of acetic acid, 2.4 kg/h of formic acid, 0.1 kg/h of water and 0.2 kg/h of high boilers was discharged at a temperature of 148.7°C via line (28). The substream separated off at the top via line (24) was fed to the phase separator (25) and separated there. The organic phase obtained, comprising 177.9 kg/h of MTBE, 0.4 kg/h of acetic acid, 0.1 kg/h of formic acid and 1.8 kg/h of water, was recirculated to the extractor (7) via line (27). The stream of aqueous phase leaving the separator via line (26) was composed of 0.03 kg/h of acetic acid, 0.02 kg/h of formic acid, 7.8 kg/h of water and 0.4 kg/h of MTBE.

At the bottom of the distillation column (29), a stream comprising 12.5 kg/h of acetic acid, 0.01 kg/h of formic acid and 0.1 kg/h of high boilers was taken off at a temperature of 154.2°C via line (31). At the bottom of the pure acetic acid column (5), a stream comprising 0.04 kg/h of acetic acid and 0.1 kg/h of high boilers was taken off at a temperature of 150°C via line (18).

- 19 -

The stream leaving the top of the distillation column (29) via line (19) comprised 0.01 kg/h of acetic acid, 2.4 kg/h of formic acid and 0.01 kg/h of water. A side offtake stream comprising 0.05 kg/h of acetic acid, 0.8 kg/h of formic acid and 0.1 kg/h of water was taken from the column (29) via line (35).

The aqueous stream leaving the bottom of the solvent stripping column (11) via line (13) comprised 48.5 kg/h of water, 0.3 kg/h of acetic acid, 0.08 kg/h of formic acid and 0.6 kg/h of high boilers. The return stream of organic phase to the extractor via line (14) from the phase separation vessel (9) of the solvent stripper (11) was composed of 1.7 kg/h of MTBE, 0.01 kg/h of acetic acid, 0.01 kg/h of formic acid and 0.05 kg/h of water.

Fractionation of the crude acid mixture into 1.6 kg/h of 98.6% purity by weight formic acid, 12.5 kg/h of 99.99% purity by weight acetic acid and 49.4 kg/h of 98.1% purity by weight water required, without preheating of the feed upstream of the distillation columns, the following energy input:

bottom heating of the solvent distillation column (8): 22.5 kW

bottom heating of the separation column (29): 10 kW

bottom heating of the pure acetic acid column (5): 4 kW

- 20 -

bottom heating of the solvent stripping column (11): 4.5 kW

The total of 41 kW corresponds to 2.9 kW per kg of acid.

Claims:

1. Process for the separation and purification of an aqueous mixture comprising the main components acetic acid, formic acid and high boilers by extraction with a solvent in a circulation process, which comprises feeding the raffinate stream containing a major part of the water to a solvent stripping column (11) for removal of the water and conveying the extract stream to a solvent distillation column (8) from which, in a first step, a mixture (A) comprising water and solvent is separated off via the top and a mixture (B) comprising acetic acid, formic acid and high boilers is separated off via the bottom, separating the formic acid off from the mixture (B) in column (29) and subsequently fractionating the remaining mixture (B) into pure acetic acid and high boilers in an acetic acid distillation column, and conveying the mixture (A) to a phase separator from which the aqueous phase containing residual solvent is recirculated to the solvent stripping column (11) and the organic phase is recirculated to the extractor (7).
2. Process according to Claim 1, characterized in that the solvent distillation column (8) is operated under atmospheric pressure.

3. Process according to Claim 1, characterized in that the solvent distillation column (8) is operated under a superatmospheric pressure of from $1 \cdot 10^5$ to $50 \cdot 10^5$ Pa.
4. Process according to any of Claims 1 to 3, characterized in that the extractor is operated in one or more stages.
5. Process according to any of Claims 1 to 4, characterized in that the solvent circuit in the extractor runs countercurrent to the crude acid.
6. Process according to any of Claims 1 to 5, characterized in that the solvent used comprises saturated, unsaturated and/or cyclic hydrocarbons having from 4 to 8 carbon atoms.
7. Process according to any of Claims 1 to 5, characterized in that the solvent used is one or more compounds selected from the group consisting of ethers, esters, ketones, hydrocarbons and alcohols.
8. Process according to any of Claims 1 to 7, characterized in that the solvent used is one or more compounds selected from the group consisting of methyl tert-butyl ether, diisopropyl ether, di-n-propyl ether, ethyl butyl ether, ethyl acetate and isopropyl acetate.
9. Process according to any of Claims 1 to 8, characterized in that the extraction is carried out at

-23-

temperatures of from 0 to 60°C and pressures of from $1 \cdot 10^5$ to $20 \cdot 10^5$ Pa.

10. Process according to any of Claims 1 to 9, characterized in that the mixing ratio of solvent to crude acid (volume/volume) is from 0.5 to 20.

11. Process according to any of Claims 1 to 10, characterized in that the intermediate distillation column (29) is operated at a pressure of from $1 \cdot 10^5$ Pa to $50 \cdot 10^5$ Pa.

12. Process according to any of Claims 1 to 11, characterized in that the solvent distillation column (8) is operated in such a way that small amounts of water remain in the product stream.

13. Process according to any of Claims 1 to 12, characterized in that the intermediate distillation column (29) is equipped with a side offtake at which a substream is taken off.

14. Process according to any of Claims 1 to 13, characterized in that the mixture (B) comprising the components acetic acid, formic acid, high boilers and residual water is fractionated in an intermediate distillation column (29) into a bottom product which is free of formic acid and comprises acetic acid and high boilers and a mixed top product comprising formic acid, water and small amounts of acetic acid, where the bottom product from column

(29) is fractionated in a downstream acetic acid distillation column (5) into pure acetic acid and high boilers and the top product from column (29) is fed to a pure formic acid distillation column (33) where it is fractionated into pure formic acid as top product and a mixed bottom product comprising acetic acid, formic acid and water which is recirculated to the extract stream to the solvent distillation column (8).

15. Process according to Claim 14, characterized in that the pure formic acid distillation column (33) is operated at a pressure which is from $0.1 \cdot 10^5$ to $25 \cdot 10^5$ Pa lower than that in the intermediate distillation column (29).

16. Process according to any of Claims 1 to 15, characterized in that the heat of condensation in the distillation column (29) is used for heating the formic acid distillation column (33) and/or the solvent distillation column (11).

17. Process according to any of Claims 1 to 16, characterized in that the heat of reaction of the upstream reaction is used for heating one or more of the solvent distillation column (8), the distillation column (29), the acetic acid distillation column (5) and the formic acid distillation column (33).

[illegible]

(10) Internationale Veröffentlichungsnummer
WO 01/07391 A1

(72) Erfinder; und
(75) Erfinder/Anmelder *(nur für US):* RÜDINGER, Christoph [DE/DE]; Moosbichlstrasse 26, D-82319 Starnberg (DE). VOIT, Harald, Herbert [DE/DE]; Georgenstrasse 7, D-84571 Reischach (DE). HALLMANN, Michael [DE/AT]; Duttendorf 103, A-5122 Hochburg-Ach (AT). GÜNALTAŞ, Mehmet [TR/DE]; Heckenweg 12, D-84547 Emmerting (DE). REIL, Barbara [DE/DE]; Heufelderweg 23, D-84547 Emmerting (DE). EBERLE, Hans-Jürgen [DE/DE]; Alfred-Kubin-Weg 44, D-81477 München (DE).

(74) Anwälte: SCHUDERER, Michael usw.; Wacker-Chemie GmbH, Zentralbereich PML, Hanns-Seidel-Platz 4, D-81737 München (DE).

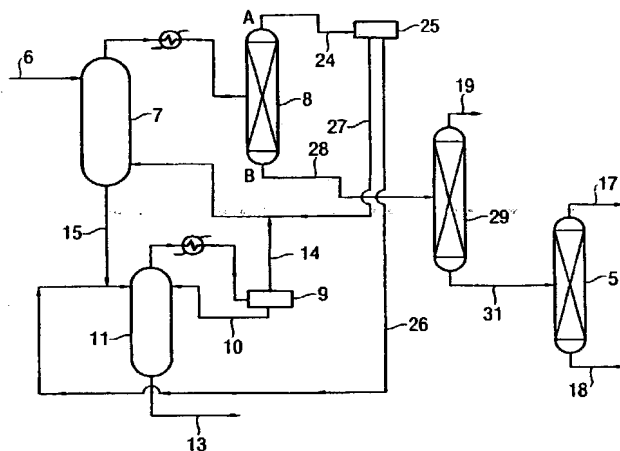
(81) **Bestimmungsstaaten (national):** BR, CN, JP, MX, NO, US.

[Fortsetzung auf der nächsten Seite]

(30) Angaben zur Priorität:
199 34 410.8 22. Juli 1999 (22.07.1999) DE

(71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme von US): CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE GMBH [DE/DE]; Zielstattstrasse 20, D-81379 München (DE).

(54) Bezeichnung: VERFAHREN ZUR TRENNUNG UND REINIGUNG EINES WÄSSRIGEN GEMISCHES AUS DEN HAUPTKOMPONENTEN ESSIGSÄURE UND AMEISENSÄURE



(57) Abstract: The invention relates to a method for separating and purifying an aqueous mixture that mainly consists of acetic acid, formic acid and high-boiling substances by extraction with a solvent in a cyclic process. The inventive method is characterized in that the flow of raffinate is fed to a solvent stripping column (11) with the major part of the water in order to remove the water from the cycle. The flow of extract is fed to a solvent recovery distillation column (8). In a first step, a mixture (A) that consists of water and solvent, is separated by overhead distillation. A mixture (B) that consists of acetic acid, formic acid and high-boiling substances is separated via a sump. Once the formic acid is removed in a column (29), mixture (B) is separated in an acetic acid distillation column to give pure acetic acid and high-boiling substances. Mixture (A) is fed to a phase separator and the aqueous phase is returned to the solvent stripping column (11) together with any residual portions of the solvent while the organic phase is returned to the extractor (8).

[Fortsetzung auf der nächsten Seite]

WO 01/07391 A1

1/3

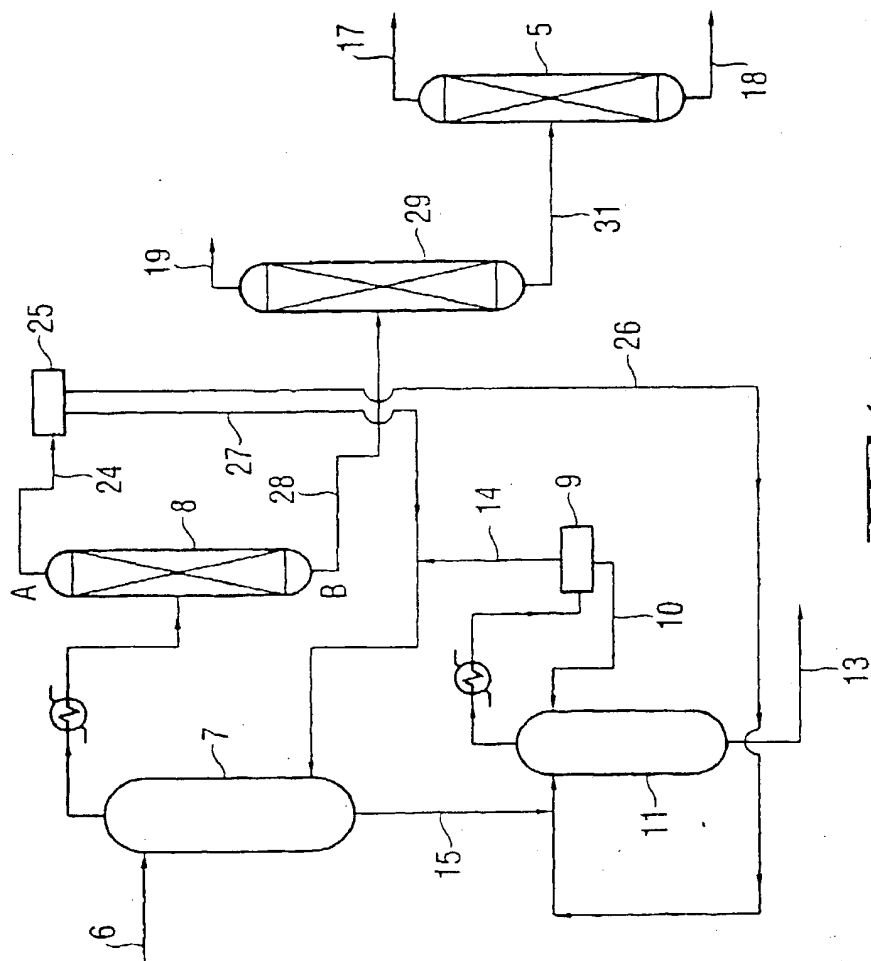


Fig. 1

2 / 3

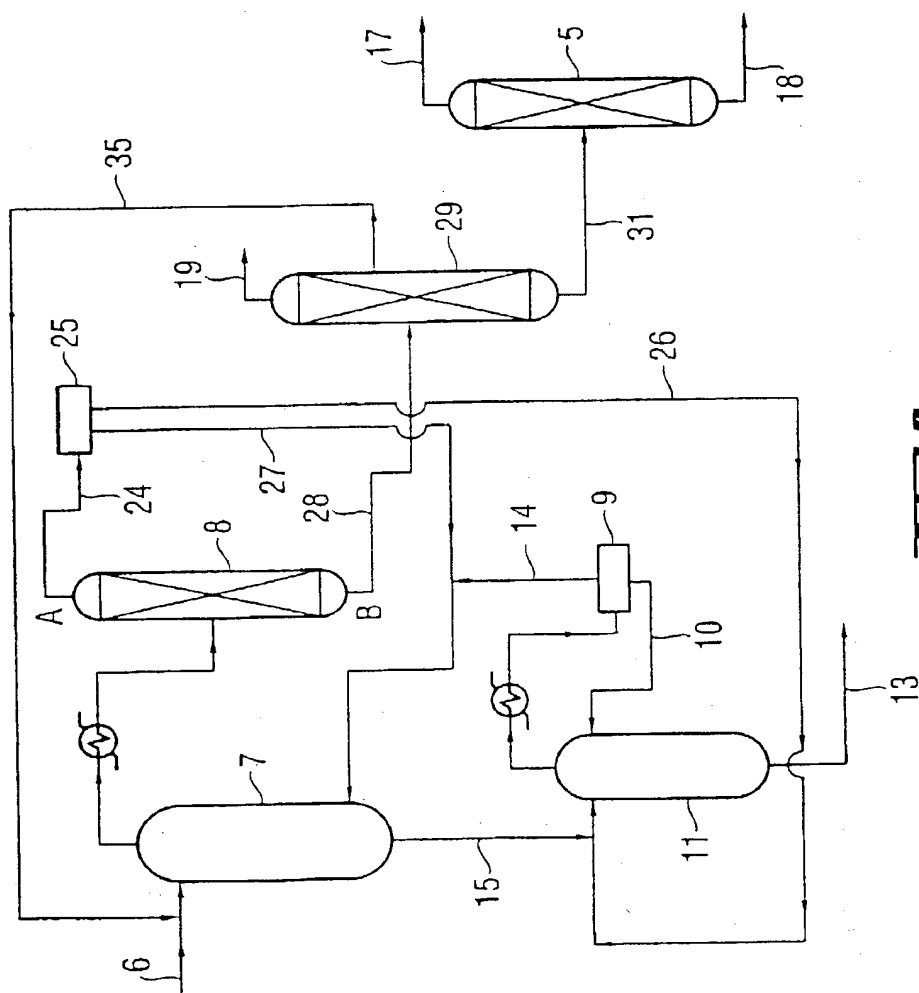


Fig. 2

3 / 3

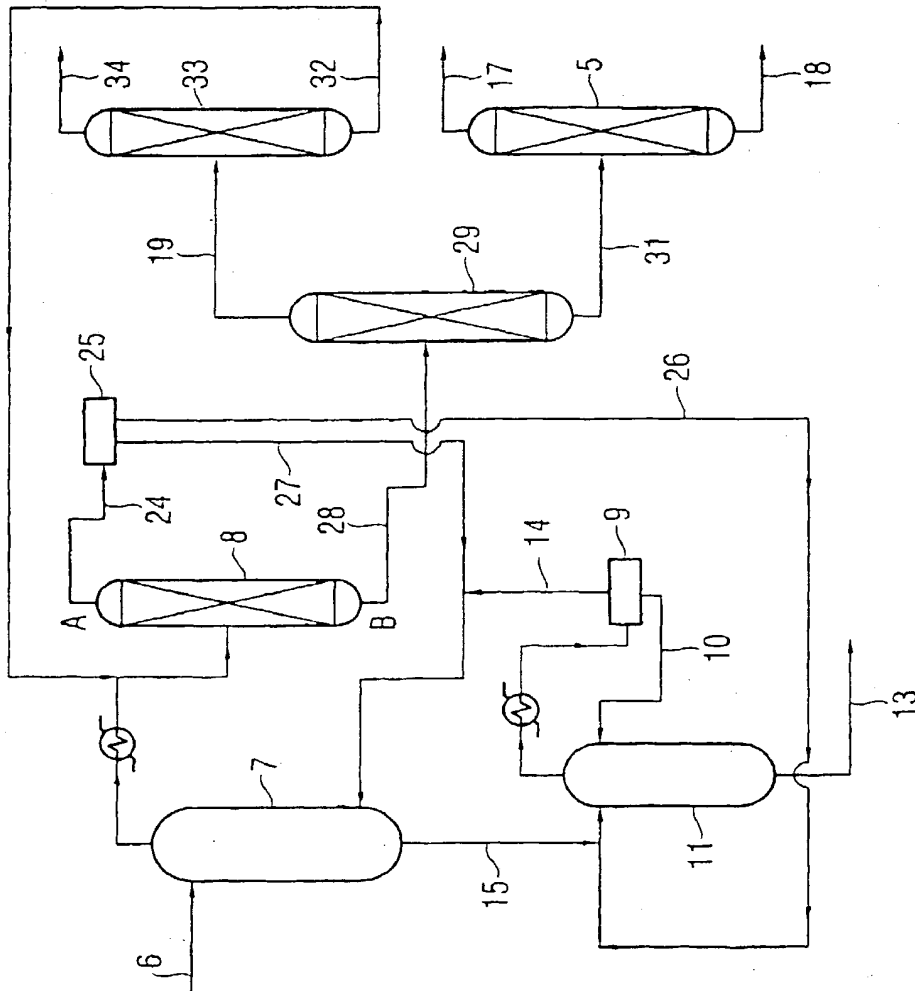


Fig. 3

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PROCESS FOR THE SEPARATION AND PURIFICATION OF AN AQUEOUS MIXTURE COMPRISING THE MAIN COMPONENTS ACETIC ACID AND FORMIC ACID

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Serial No. _____

on _____,

and was amended

on _____ (if applicable).

☒ was filed as PCT international application

Number PCT/EP00/06092

on June 29, 2000

and was amended under PCT Article 19

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
Germany	199 34 410.8	22 July 1999	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(Includes Reference to PCT International Applications)

ATTORNEY'S DOCKET NUMBER
RÜDINGER ET AL -5 (PCT)

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS			STATUS (Check One)		
U.S. APPLICATION NUMBER	U.S. FILING DATE		PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)			

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration numbers):
ALLISON C. COLLARD, Registration No. 22,532;
EDWARD R. FREEDMAN, Registration No. 26,048;
ELIZABETH COLLARD RICHTER, Registration No. 35,103
KURT KELMAN, Registration No. 18,628
FREDERICK J. DORCHAK, Registration No. 29,298
WILLIAM C. COLLARD, Registration No. 38,411
REINE H. GLANZ, Registration No. 46,728

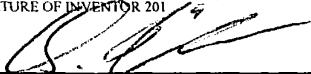
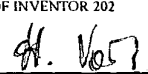
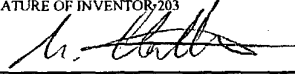
Send Correspondence to: **COLLARD & ROE, P.C.**
1077 Northern Boulevard
Roslyn, New York 11576

Customer No. **25889**

Direct Telephone Calls to:
(name and telephone number)
(516) 365-9802

100	2	FULL NAME OF INVENTOR	FAMILY NAME <u>RÜDINGER</u>	FIRST GIVEN NAME <u>CHRISTOPH</u>	SECOND GIVEN NAME
	0	RESIDENCE & CITIZENSHIP	CITY <u>STARNBERG</u>	STATE OR FOREIGN COUNTRY <u>GERMANY DEX</u>	COUNTRY OF CITIZENSHIP <u>GERMANY</u>
	1	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>MOOSBICHLSTR. 26</u>	CITY <u>D-82319 STARNBERG</u>	STATE & ZIP CODE/COUNTRY <u>D-82319/GERMANY</u>
200	2	FULL NAME OF INVENTOR	FAMILY NAME <u>VOIT</u>	FIRST GIVEN NAME <u>HARALD</u>	SECOND GIVEN NAME <u>HERBERT</u>
	0	RESIDENCE & CITIZENSHIP	CITY <u>REISCHACH</u>	STATE OR FOREIGN COUNTRY <u>GERMANY DEX</u>	COUNTRY OF CITIZENSHIP <u>GERMANY</u>
	2	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>GEORGENSTR. 7</u>	CITY <u>D-84571 REISCHACH</u>	STATE & ZIP CODE/COUNTRY <u>D-84571/GERMANY</u>
300	2	FULL NAME OF INVENTOR	FAMILY NAME <u>HALLMANN</u>	FIRST GIVEN NAME <u>MICHAEL</u>	SECOND GIVEN NAME
	0	RESIDENCE & CITIZENSHIP	CITY <u>HOCHBURG-ACH</u>	STATE OR FOREIGN COUNTRY <u>AUSTRIA ATX</u>	COUNTRY OF CITIZENSHIP <u>AUSTRIA</u>
	3	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>DUTTENDORF 103</u>	CITY <u>A-5122 HOCHBURG-ACH</u>	STATE & ZIP CODE/COUNTRY <u>A-5122/AUSTRIA</u>

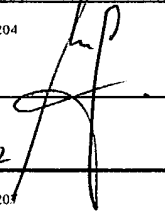
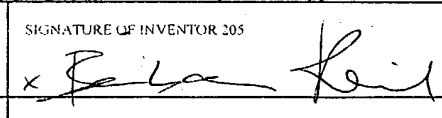
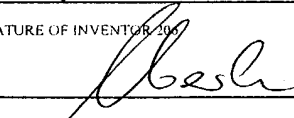
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201 X 	SIGNATURE OF INVENTOR 202 X 	SIGNATURE OF INVENTOR 203 X 
DATE X <u>5. NOV. 2001</u>	DATE X <u>9. Nov. 2001</u>	DATE X <u>8. Nov. 2001</u>

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (Includes Reference to PCT International Applications)				ATTORNEY'S DOCKET NUMBER RÜDINGER ET-AL -5 (PCT)	
I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.					
(Application Number)			(Filing Date)		
I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:					
PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:					
U.S. APPLICATIONS			STATUS (Check One)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)			
PCT/EP00/06092	June 29, 2000	10/009,507		X	
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration numbers):					
ALLISON C. COLLARD, Registration No. 22,532; EDWARD R. FREEDMAN, Registration No. 26,048; ELIZABETH COLLARD RICHTER, Registration No. 35,103			KURT KELMAN, Registration No. 18,628 FREDERICK J. DORCHAK, Registration No. 29,298 WILLIAM C. COLLARD, Registration No. 38,411 ROBERT W. GRIFFITH, Registration No. 48,956		
Send Correspondence to: COLLARD & ROE, P.C. 1077 Northern Boulevard Roslyn, New York 11576			Customer No. 25889		Direct Telephone Calls to: (name and telephone number) (516) 365-9802
2	FULL NAME OF INVENTOR	FAMILY NAME RÜDINGER	FIRST GIVEN NAME CHRISTOPH	SECOND GIVEN NAME	
0	RESIDENCE & CITIZENSHIP	CITY STARNBERG	STATE OR FOREIGN COUNTRY GERMANY	COUNTRY OF CITIZENSHIP GERMANY	
1	POST OFFICE ADDRESS	POST OFFICE ADDRESS MOOSBICHLSTR. 26	CITY D-82319 STARNBERG	STATE & ZIP CODE/COUNTRY D-82319/GERMANY	
2	FULL NAME OF INVENTOR	FAMILY NAME VOIT	FIRST GIVEN NAME HARALD	SECOND GIVEN NAME HERBERT	
0	RESIDENCE & CITIZENSHIP	CITY REISCHACH	STATE OR FOREIGN COUNTRY GERMANY	COUNTRY OF CITIZENSHIP GERMANY	
2	POST OFFICE ADDRESS	POST OFFICE ADDRESS GEORGENSTR. 7	CITY D-84571 REISCHACH	STATE & ZIP CODE/COUNTRY D-84571/GERMANY	
2	FULL NAME OF INVENTOR	FAMILY NAME HALLMANN	FIRST GIVEN NAME MICHAEL	SECOND GIVEN NAME	
0	RESIDENCE & CITIZENSHIP	CITY HOCHBURG-ACH	STATE OR FOREIGN COUNTRY AUSTRIA	COUNTRY OF CITIZENSHIP AUSTRIA	
3	POST OFFICE ADDRESS	POST OFFICE ADDRESS DUTTENDORF 103	CITY A-5122 HOCHBURG-ACH	STATE & ZIP CODE/COUNTRY A-5122/AUSTRIA	
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.					
X	SIGNATURE OF INVENTOR 201		X	SIGNATURE OF INVENTOR 202	
X	DATE 21.06.2002		X	DATE 14.06.2002	
X	SIGNATURE OF INVENTOR 203		X	DATE 14.06.2002	

2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
4	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
		HECKENWEG 12	D-84547 EMMERTING	D-84547/GERMANY
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
5	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
		HEUFELDERWEG 23	D-84547 EMMERTING	D-84547/GERMANY
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
6	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
		ALFRED-KUBIN-WEG 44	D-81477 MÜNCHEN	D-81477/GERMANY
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
7	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
8	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
9	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 204	SIGNATURE OF INVENTOR 205	SIGNATURE OF INVENTOR 206
x 	x 	x 
DATE	DATE	DATE
x 18.06.2002	x 2002-06-05	x 2002-06-21
SIGNATURE OF INVENTOR 207	SIGNATURE OF INVENTOR 208	SIGNATURE OF INVENTOR 209
DATE	DATE	DATE

400

600

2	FULL NAME OF INVENTOR	FAMILY NAME <u>GÜNAL TAY</u>	FIRST GIVEN NAME <u>MEHMET</u>	SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY <u>EMMERTING</u>	STATE OR FOREIGN COUNTRY <u>GERMANY</u> <i>DEX</i>	COUNTRY OF CITIZENSHIP <u>TURKEY</u>
4	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>HECKENWEG 12</u>	CITY <u>D-84547 EMMERTING</u>	STATE & ZIP CODE/COUNTRY <u>D-84547/GERMANY</u>
2	FULL NAME OF INVENTOR	FAMILY NAME <u>WILD</u>	FIRST GIVEN NAME <u>BARBARA</u>	SECOND GIVEN NAME <u>GEBORENE/NEE REIL</u>
0	RESIDENCE & CITIZENSHIP	CITY <u>EMMERTING</u>	STATE OR FOREIGN COUNTRY <u>GERMANY</u>	COUNTRY OF CITIZENSHIP <u>GERMANY</u>
5	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>HEUFELDERWEG 23</u>	CITY <u>D-84547 EMMERTING</u>	STATE & ZIP CODE/COUNTRY <u>D-84547/GERMANY</u>
2	FULL NAME OF INVENTOR	FAMILY NAME <u>EBERLE</u>	FIRST GIVEN NAME <u>HANS</u>	SECOND GIVEN NAME <u>JÜRGEN</u>
0	RESIDENCE & CITIZENSHIP	CITY <u>MÜNCHEN</u>	STATE OR FOREIGN COUNTRY <u>GERMANY</u> <i>DEX</i>	COUNTRY OF CITIZENSHIP <u>GERMANY</u>
6	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>ALFRED-KUBIN-WEG 44</u>	CITY <u>D-81477 MÜNCHEN</u>	STATE & ZIP CODE/COUNTRY <u>D-81477/GERMANY</u>
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
7	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
8	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
9	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 204 <i>[Signature]</i>	SIGNATURE OF INVENTOR 205 <i>[Signature]</i>	SIGNATURE OF INVENTOR 206 <i>[Signature]</i>
DATE <i>13. Nov. 2001</i>	DATE <i>16. M. 2001</i>	DATE <i>17. Nov. 2001</i>
SIGNATURE OF INVENTOR 207	SIGNATURE OF INVENTOR 208	SIGNATURE OF INVENTOR 209
DATE	DATE	DATE